Vietnam Journal of Chemistry, International Edition, **55**(6): 750-755, 2017
DOI: 10.15625/2525-2321.2017-00539

Effect of deposition time on gold nanodendrite porous structure and on signals of Hg(II) in environment

Pham Thi Hai Yen, Vu Hai Dang, Nguyen Hoang Anh, Vu Thi Thu Ha*
Institute of Chemistry, Vietnam Academy of Science and Technology
Received 13 October 2017; Accepted for publication 29 December 2017

Abstract

The influences of deposition time (t_{dep}) for Au nanodendrite preparation on carbon cloth electrodes on the surface structure, electrochemical behavior and voltammetric signal for Hg(II) detection have been studied. The obtained results showed that from 60 s to 300 s, the longer deposition time, the larger dendrite length as well as the more increased density of dendrite structure became. Calculated from data showed that the electroactive surface area approached to the maximum value of 3.686 cm^2 with t_{dep} = 300 s. The typical electrochemical behaviour of the prepared electrodes was mass transfer diffusion to the electrode surface and being considered as planar diffusion. Using DPASV technique, the peak height of Hg(II) could appoach to 52 µA with t_{dep} = 60 s.

Keywords. Gold nanodendrite, deposition time, surface structure, electrochemical properties, mercury.

1. INTRODUCTION

Recently, a variety of electrode materials have been manufactured for electrochemical analysis such as platinum [1], gold [2, 3], mercury [4, 5] and carbon-based materials [6, 7] with various structures in different sizes. These electrodes were fabricated for the purpose of providing interesting properties: durability, high selectivity, low limit of detection (LOD), wide linear range and being able to be used in special conditions: small volume, high viscosity, weak electrolyte etc. In recent research, microelectrodes and electrodes modified with organic compounds, polymers or nanomaterials have gained a special attention of researchers.

Among numerous types of materials, gold has been widely used in fabricating electrodes with different structures that perfectly matched with specific experiment's purposes and requirements due to its significant chemical and physical characteristics such as flexible, chemically inert, easily produced by electrochemical methods. Gold electrodes can be made in a wide range of scales that are gold disk at millimeter-scale [3, 8, 9], gold microwire [10] or microdisk electrodes and gold nanostructures (nanoparticles, nanoporous ...) [11, 12].

Gold disk electrodes are the simpliest and most common form of gold electrodes being used [3]. Besides, the microelectrodes with many outstanding features have also been studied. In 2004, G. Billon and C. M. G. Van den Berg [2] confirmed the quasi-stable state of gold microwire electrode and applied for quantification of Pb(II), LOD was 14.5 ppt. In 2006, Olga Ordei [13] demonstrated that the fabricated microarray electrode has the property of stable state current. Linear range of Hg (II) analysis on this electrode was 10÷200 ppb.

In recent decades, nanoelectrodes were used with the aim to increase the sensitivity of the analysis. In 2005, Xuan Dai and Richard G. Compton [14] used the gold nanoparticles electrode (AuNP) to raise the ability of As(III) detection. In 2012, in the research of Minh Phuong Ngoc Bui [15], AuNP was modified on carbon nanotube substrate to analyze Pb (II) and Cd (II).

Beside nanoparticles structure, gold nanoelectrodes are also made in other forms such as nanoporous (np-Au) [16], nanodendrite (AuND) [11] with the aim of increasing the electrode active area, hence the sensitivity of the analysis increases significantly. In 2012, Michael D. Scanlon [16] modified GC electrode by Au nanoporous (np-Au) layer, the active area of the np-Au electrode was 28 times greater than the geometric surface area. In 2011, Tran Ngoc Huan's group [11] showed that peak current obtained when using AuND/Pt electrode for As(III) analysis increased significantly in comparison with using AuNP/Pt (40 times higher) and especially in comparison with gold disk electrode.

Continuation to our previous studies of AuND electrodes [17], in this work, we focused on the effects of deposition time of AuND (t_{dep}) on

morphological structure of electrode surface, their electrochemical properties as well as mercury signal measured on these electrodes. The carbon fiber cloth was used as the substrate-electrode because of its wide electrochemical range and other characters: flexible, cheap and easily made into electrodes with a certain size.

2. EXPERIMENTAL

2.1. Materials, reagents and apparatus

Materials and reagents: Carbon fiber cloth (W0S1002) was obtained from Nara Celltech Corp., Korea. Solutions of 1000 ppm H_2SO_4, CH_3COCH_3, C_2H_5OH, $HAuCl_4$, KI, NH_4Cl, $K_3[Fe(CN_6)]$, K_2HPO_4, KH_2PO_4, KCl, HCl, $Hg(NO_3)_2$, ultrapure water, etc. were prepared for the experiment. All reagents were purchased from Merck (German) and Sigma (America) without any further purification.

Apparatus: Scanning electron microsope (SEM) images were taken from Hitachi S-4800 (Japan) with a primary electron beam accelerated by 0.5÷30 kV potential. Preparation of AuND and all the electrochemical measurements was carried out by CPA-HH* instrument (a custom-made multi-function potentialgalvanostat manufactured at the Institute of Chemistry, Hanoi, Vietnam) with three-electrode system: Ag/AgCl reference electrode, Pt counter electrode and working electrode made of investigated materials. Differential Pulse Anodic Stripping Voltametry technique (DPASV) was used to record signals of Hg(II) in electrolyte cell.

2.2. Preparation of AuND/Ccloth

To form carbon cloth electrode, a piece of (6×6) mm carbon fiber cloth was prepared and gently washed with double-distilled water and acetone. Then it was electrochemically cleaned by applying a potential of -1 V in 0.5 M H_2SO_4 for 300 s.

To fabricate gold nanodendrite structure on carbon fiber cloth, galvanostatic techniques was used with a current of -70 mA in a mixture of 20 mM $HAuCl_4$, 1 mM KI, 5 M NH_4Cl and 0.5 M H_2SO_4. The electrodeposition time used to form AuND on C_{cloth} electrode was examined over different time values 60, 120, 180, 240, 300 & 360 s.

Produced electrode was then rinsed by mixed solution of acetone and distilled water (1:1) several times to eliminate the chemical remained on the electrode surface.

2.3. Electrochemical measurement

The diffusion property and reversibility behaviors of electrochemical reactions on produced electrodes was examined in solution of 0.5 M $K_3[Fe(CN_6)]$ made in 0.1 M phosphorus buffer solution (PBS) at pH = 7. DPASV technique was used to detect mercury signals in standard solution of 10 ppb Hg made in 0.1 M KCl + HCl at pH = 3. The mercury accumulation was carried out at potential of 0 V for 180 s, the stripping range was from 0.3 V to 0.9 V.

3. RESULTS AND DISCUSSION

3.1. Morphology of AuND/C_{cloth} surface

The surface structure of AuNDs/C_{cloth} with different electrodeposition durations were showed in SEM images (figure 1). The obtained resutls show that with the presence of I^- and NH_4^+ reagents [17] produced gold electrodes would have nanodendrite porous structure. With the variety of t_{dep}, the gold layer was formed on electrodes surface with differences in density, complexity of gold branches. However, general size of main branches were around 200 nm, then on these adjacent branches smaller size branches (< 100 nm) could be formed depending on deposition conditions.

The 60-second electrodeposition produced a simple nanodendrite structure consisting of several small branches along the main Au column that layer-by-layer created porosity for the fabricated gold. With longer electrodeposition duration, the nanodendrite structures became more complicated. There were many smaller dendrite combinations created base on previous gold branches and the dendrite structure became more obvious. When electrodeposition time reached 360 s, produced nanodendrites were so dense that they aggreated to gold bulk, fill up empty spaces between branches, thus decreasing the porosity of the electrodes. Therefore, the nanodendrites structure was just partly observed on the electrodes surface.

3.2. Electrochemical characterization of AuND/C_{cloth} electrodes

Due to the complicated structure of nanodendrites surface (figure 1), electrochemical reactions, which happened on the boundary between electrodes surface and the solution, mainly depend on characterization of dendrite struture growing on the electrodes. Electrochemical properties of produced electrodes were examined in solution of 5 mM $K_3[Fe(CN)_6]$ / 0.1 M PBS at pH = 7.

Cyclic voltammograms (figure 2) acquired with different scan rates on AuND/C_{cloth} electrodes show peak shape that characterizes planar diffusion of

electroactive substances to electrodes. This is because the surface of examined electrode was formed by layers of nanodendrites leading to the overlap of individual diffusion zones of gold branches over the electrodes as electrochemical reactions occurred.

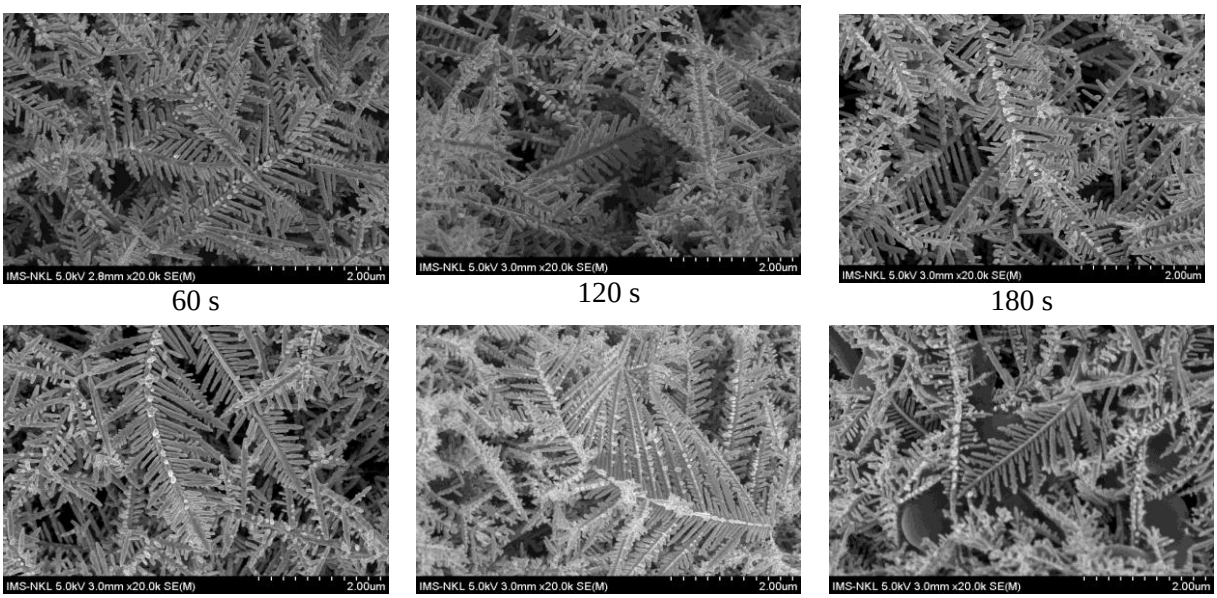

Figure 1: SEM images of AuND/C_{cloth} prepared by using various electrodeposition durations

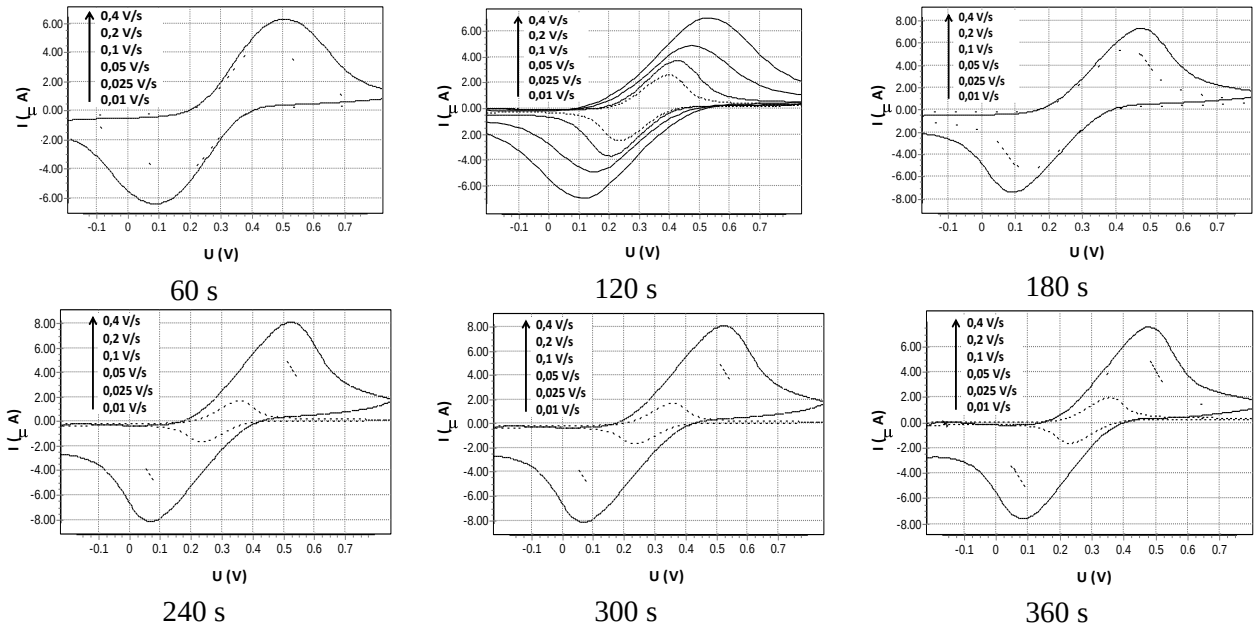

Figure 2: CVs recorded in 5 mM $K_3[Fe(CN)_6]$ / 0.1 M PBS pH = 7 on AuNDs/C_{cloth} prepared in different t_{dep} at various scan rate: from 0.01 V/s to 0.4 V/s

Oxidation peak (i_{pa}) and reduction peak (i_{pc}) obtained from all prepared AuNDs/C_{cloth} in this study were proportional to the square root of the scan rate and the ratio $i_{pa}/i_{pc} \approx 1$ in all measurements. This indicated that on studied electrodes, redox reactions Fe^{3+} + 1e ↔ Fe^{2+} were successfully occurred in both side of the reaction and it was in agreement with previous publication [18].

The difference of peak potential (ΔE) measured on each studied electrodes were gradually increased as the scan rate reached higher values. This is due to the increase of voltage drop when current (i_p) rises and i_p is proportional to the square root of the scan rate.

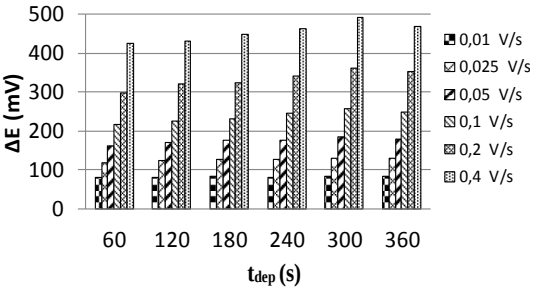

Figure 3: The graph describes of scan rate dependence of ΔE on AuND/C_{cloth} electrodes with different t_{dep}

Consider over a certain scan rate, as the t_{dep} raise from 60 s to 360 s, surface area of electrodes was also altered causing the acquired current to vary. As a result, the distance between the two peaks increased with deposition time of gold and reached the maximum when t_{dep} was 300 s. This figure decreased when t_{dep} reached 360 s. This can be explained that the electrode surface area went up gradually when t_{dep} rise from 60 s to 300 s and went down when t_{dep} was 360 s.

The active surface area A_{act}, of studied electrodes followed directly to *Randle-Sevcik* equation:

$$I_p = (2{,}69.10^5).\, n^{3/2}.\, A.D^{1/2}.\, C.\nu^{1/2}$$

Where, i_p is the peak current, A is the active surface area (cm^2), D is the diffusion coefficient (cm^2/s), C is the molar concentration (mol/cm^3), ν is the scan rate (V/s), n is the electron transferred in redox reaction.

Peak current was obtained from CVs, n = 1, C = 5.10^{-6} mol/cm^3, ν = 0.1 V/s, D = 7.5×10^{-6} cm^2/s [19]. The caculated A_{act} are shown in table 1.

Table 1: The electrochemical active surface area of AuND/C_{cloth} electrodes with different t_{dep} values

Deposition durations	60 s	120 s	180 s	240 s	300 s	360 s
i_{pc} (mA)	3.40	3.69	3.91	4.07	4.30	4.03
A_{act} (cm^2)	2.914	3.163	3.351	3.488	**3.686**	3.454
$A_{geographic}$ bare electrode (cm^2)	0.720					

From obtained results, the electrochemical active surface area of AuND/C_{cloth} electrode was highest at 300 s deposition time. This record is consistent with SEM images on 3.1 section.

That is when t_{dep} changed from 60 s to 300 s, due to the increasing in the amount and complexity of gold dendrites structure, electrochemical surface area also increased. However, as the electrodeposition time reached to 360 s, this porous structure was filled up by deposited gold leading to formation of dense gold bulk and decrease of electrode active surface area (figure 1).

3.3. Electrochemical signals of Hg(II) on AuND/C_{cloth} electrodes

Figure 4 shows the DPASVs of mercury detection on AuND electrodes and the relation between peak currents and t_{dep}. It is clear that the mercury signal was highest with t_{dep} = 60 s (i_p = 52 µA). The peak current decreased when the electrodeposition time increased to 180 s but slightly rose in relation to higher t_{dep} before fell down when t_{dep} reached to 360 s.

This change is due to the complexity of surface structure of dendrite electrodes. The surface of the electrode fabricated for 60 s contained simple branches which increase dramatically acting area.

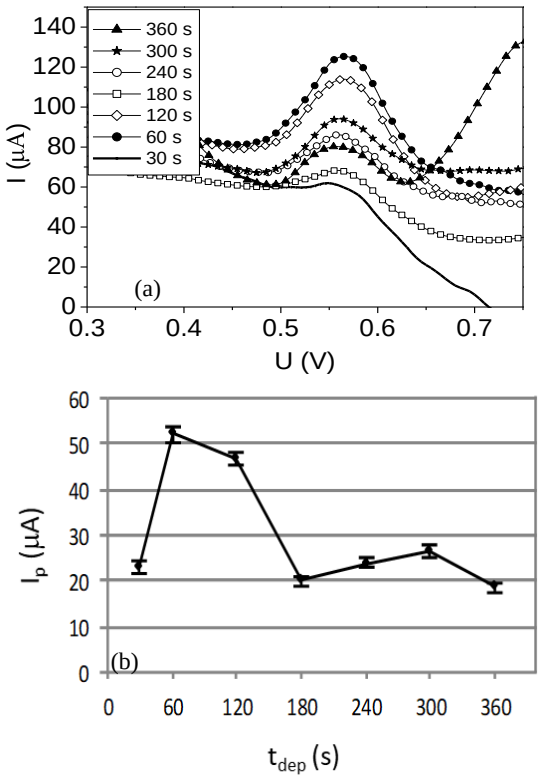

Figure 4: ASDPV voltammograms (a) and graph describing the dependence of 10 ppb mercury peak on deposition time of AuND/C_{cloth} electrode (b) in solution of 0.1 M KCl and HCl pH 3

However, when the deposition time increased, the density of branches increased, the diffusion of mercury ions into deeper layer became harder.

Consequently, the surface area increased but the signal decreased.

The variation between 180 s and 360 s can be explained by SEM images: because of the increase of the length of branches on external layer, the peak current slightly went up when the deposition time increased from 180 s to 300 s. With 360 s deposition, the branches became denser, the porosity dropped as well as the surface area (table 1), thus peak height went down also.

4. CONCLUSION

Variation of surface morphology and electrochemical characterization of gold nanodendrites electrodes with gold deposition duration has been investigated. Obtained results show that the size of gold branches and density of dendrite combinations increased with the rising of deposition duration, hence, the surface acting area of the electrodes are changed. The maximum area was acquired when deposition time reached 300 s. All the studied electrodes were qualified in delivering electrochemical reactions as well as detecting Hg(II) in aquatic environment with 52 µA being the highest current measured in 60 s deposition time.

Acknowledgements. *The present work was financially supported by Institute of Chemistry, VAST, code No. VHH.2017.1.01. The authors would like to thank TWAS under Research Grant No. 15-122 RG/CHE/AS_G – FR3240287034.*

REFERENCES

1. Lin Cui, Jie Wu & Huangxian Ju. *Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials*, Biosensors and Bioelectronics, **63**, 276-286 (2015).
2. Gabriel Billon & Constant M G van den Berg. *Gold and Silver Micro-Wire Electrodes for Trace Analysis of Metals*, Electroanalysis, **16(19)**, 1583-1591 (2004).
3. Ricardo D. Riso, Matthieu Waeles, Philippe Monbet, et al. *Measurements of trace concentrations of mercury in sea water by stripping chronopotentiometry with gold disk electrode: influence of copper*, Analytica Chimica Acta, **410(1-2)**, 97-105 (2000).
4. Kevin C. Honeychurch. *Screen-printed Electrochemical Sensors and Biosensors for Monitoring Metal Pollutants*, Insciences J., **2(1)**, 1-51 (2012).
5. Grigore Munteanu, Sorin Munteanu & David O. Wipf. *Rapid determination of zeptomole quantities of Pb^{2+} with the mercury monolayer carbon fiber electrode*, Journal of Electroanalytical Chemistry, **632(1-2)**, 177-183 (2009).
6. Muniyandi Rajkumar, Soundappan, Thiagarajan et al. *Electrochemical Detection of Arsenic in Various Water Samples*, Int. J. Electrochem. Sci., **6**, 3164 - 3177 (2011).
7. Bengi Uslu & Sibel A. Ozkan. *Solid Electrodes in Electroanalytical Chemistry: Present Applications and Prospects for High Throughput Screening of Drug Compounds*, Combinatorial Chemistry & High Throughput Screening, **10**, 495-513 (2007).
8. Y. Bonfil, M. Brand & E. Kirowa-Eisner. *Trace determination of mercury by anodic stripping voltammetry at the rotating gold electrode*, Analytica Chimica Acta, **424(1)**, 65-76 (2000).
9. Agnese Giacomino, Ornella Abollino, Mery Malandrino et al. *Parameters affecting the determination of mercury by anodic stripping voltammetry using a gold electrode*, Talanta, **75(1)**, 266-273 (2008).
10. Georgina M. S. Alves, Júlia M. C. S. Magalhães, Pascal Salaün et al. *Simultaneous electrochemical determination of arsenic, copper, lead and mercury in unpolluted fresh waters using a vibrating gold microwire electrode*, Analytica Chimica Acta, **703(1)**, 1-7 (2011).
11. Tran Ngoc Huan, Thothadri Ganesh, Kwang Soo Kim et al. *A three-dimensional gold nanodendrite network porous structure and its application for an electrochemical sensing*, Biosensors and Bioelectronics, **27(1)**, 183-186 (2011).
12. Tribidasari Anggraningrum Ivandini1, Lany Wijaya, Jarnuzi Gunlazuardi et al. *Modification of Gold Nanoparticles at Carbon Electrodes and the Applications for Arsenic (III) Detections*, Makara Journal of Science, **16(1)**, 9-14 (2012).
13. Olga Ordeig, Craig E. Banks, Javier del Campo, et al. *Trace Detection of Mercury(II) Using Gold Ultra-Microelectrode Arrays*, Electroanalysis, **18(6)**, 573-578 (2006).
14. Xuan Dai & Richard G. Compton. *Gold Nanoparticle Modified Electrodes Show a Reduced Interference by Cu(II) in the Detection of As(III) Using Anodic Stripping Voltammetry*, Electroanalysis, **17(14)**, 1325-1330 (2005).
15. Minh-Phuong Ngoc Bui, Cheng Ai Li, Kwi Nam Han et al. *Simultaneous detection of ultratrace lead and copper with gold nanoparticles patterned on carbon nanotube thin fil*m, Analyst, **137(8)**, 1888-1894 (2012).
16. Micheál D. Scanlon, Urszula Salaj-Kosla, Serguei Belochapkine et al. *Characterization of Nanoporous Gold Electrodes for Bioelectrochemical Applications*, Langmuir, **28(4)**, 2251-2261 (2012).
17. Pham Thi Hai Yen, Vu Thi Thu Ha, Pham Khac Duy, et al. *Investigation of electrochemical properties of*

homemade nano gold electrodes and application in determination of Hg(II) at the trace levels, Vietnam Journal of Chemistry, **53(3)**, 657-662 (2015).

18. Richard G Compton & Craig E. Banks, *Understanding Voltammetry (2nd Edition)*, Imperial College Press (2010).
19. Anton Ressine, Cristina Vaz-Domínguez, Victor M. Fernandez et al. *Bioelectrochemical studies of azurin and laccase confined in three-dimensional chips based on gold-modified nano-/microstructured silicon*, Biosensors and Bioelectronics, **25(5)**, 1001-1007 (2010).

Corresponding author: **Vu Thi Thu Ha**
Institute of Chemistry
Vietnam Academy of Science and Technology
18, Hoang Quoc Viet road, Cau Giay district, Hanoi, Viet Nam
E-mail: vuthithuha503@gmail.com.